Executive Summary

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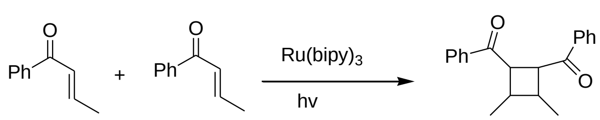
Title of research project: A Greener route towards C–C coupling reactions with metal nanocomposite under visible light.

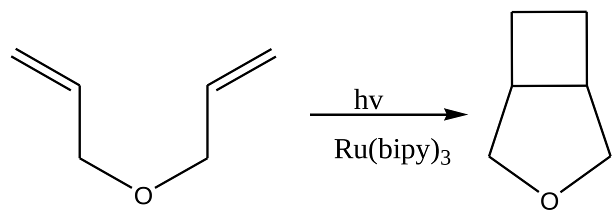
1.1 Introduction: **Part A: Designing of Photcatalyst towards Cycloaddition reaction.**

Concept of catalyst: The present work based the concept of catalyst, is chemical entity which alters rate of chemical transformation. These involves homogenous and heterogeneous catalyst. Heterogeneous catalyst is better choice since it ensures easy catalyst work up due to separation of catalyst. There are many challenges in the field of catalysis to designing of catalyst which fulfils chemoselectivity and brings about effective molecular collision during synthetic transformations. In recent days, photocatalysis becomes important emerging area which involves efficient harvesting and effective utilization of solar light through photo catalytic process has become a prime aspect of various scientific and technological developments[1]. It has encouraged us to investigate the new entities which are based on visible light driven organic transformations using a semiconducting heterogeneous nanocomposites as catalyst[2]. That afford high yield of desired product with sustain catalytic activity due minimum photo-corrosion and leaching of catalyst.

SchemeII Visble light catalysed [2π+2π] cycloaddition using ruthenium based photocatalyst.



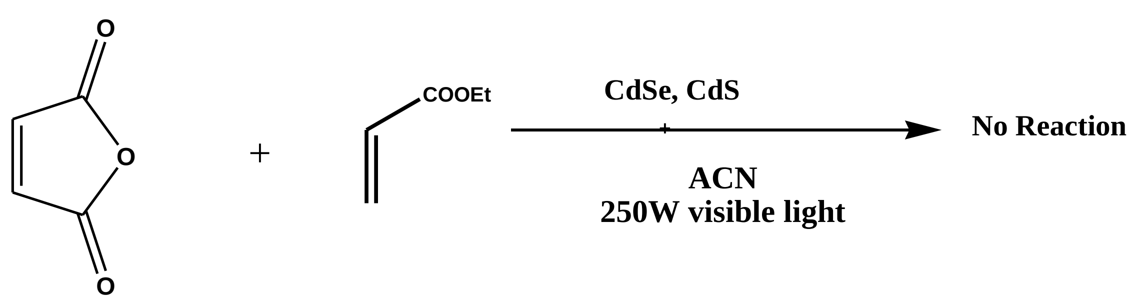
***Scheme1*:** classical intermolecular **[**2π+2π] cycloaddition based on homogenous catalyst.



Scheme1**:** classical intramolecular **[**2π+2π] cycloaddition based on homogenous catalyst.

In a classical photocycladdition reaction involves high energetic this is because inability of organic substrates like eneones to absorbs light. The present literature reveals that both intermolecular and intramolecular type of cycloaddition and C-C coupling reaction involves UV light due to high energetics. Based on this literature we thought to adopted simple stategy to design catalyst which brings about this type of conversion under visible light using Ru-based catalyst.

Conventional metal supported semiconducting heterogeneous catalysts with particle size typically on the bulk or micrometer scale are the type of catalyst that is most widely used in industry [3] . However, the energitics of these does not tuned with these reactions therefore it requires uv light which is not environmentally benign, although the advent in nanoscience and nanotechnology, the new avenues are opened to designed nano-engineered catalyst TiO_2 ,ZnO, CdSe, Cds in which the particle size is reduced to nano-range with better activity still it fails to do the expected results.



Scheme 3 : Failure of phtocycloaddition reaction using semiconducting nanocomposite.

The broad spectrum of nanostructure catalysts or solid-supported nanoprous catalysts has been applied to C-C catalytic transformations. But we are fails to achive this type of photocycloadditions.

Based on above result we had come to the conclusion to devise Ru-based polypyridyl complexes as new catalyst for the C-C bond forming reactions as well as cycloaddition reactions which will ensures reusability due to montmorillontrite as clay support.

Developments in the Synthesis of Supported RuNP's nanocomposites as Catalysts

Our approach is to immobilized nanoparticles on solid support for visible light driven catalytic c organic transformation processes such as C-C coupling and cycloaddition reactions.[5] Such bifunctional nanocomposites possessing beneficial catalytic activity due to synergism between support and nanoparticles. Designing of efficient catalysts have been core concern for the synthesis of cycloaddition based reaction with higher selectivity, better conversion and catalyst recovery that enhances "green" credentials of the process in a sustainable manner.[6]

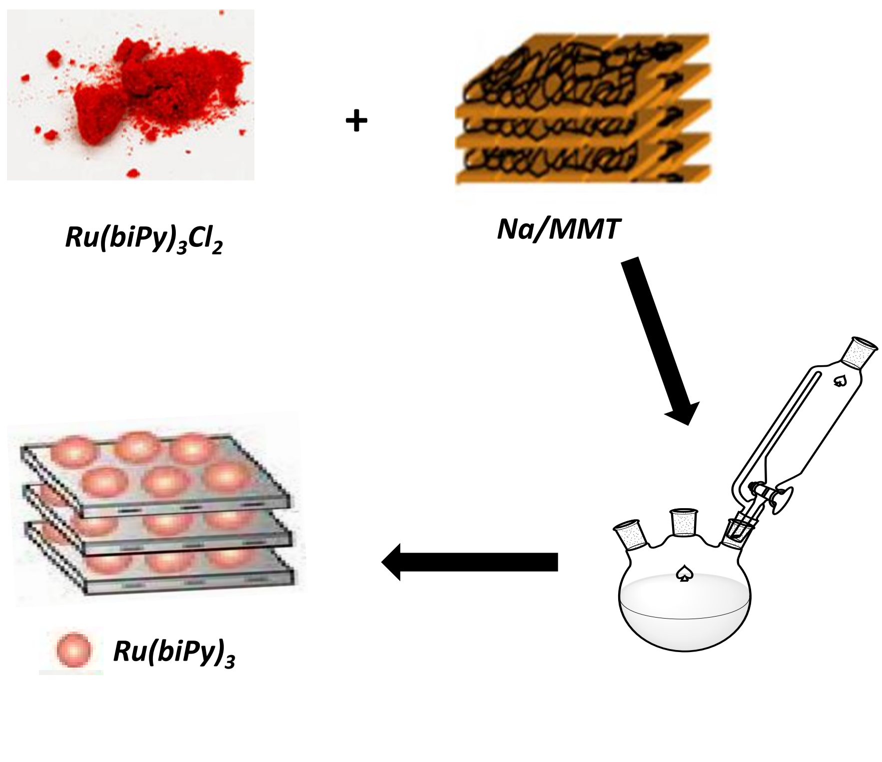


Figure 2. Ruthenium polypyridyl complexes on MMT : versatile visible light photocatalysts

This has led to the expansion of interesting materials for the specific applications in catalysis[7] A variety of different materials like carbon, polymers, clay minerals and metal oxides are used for this purpose but our choice is natural clay MMT as it generate distinct reaction sites that prevents agglomeration with providing specific adsorption sites and subsequently enhances reusability and the service life of the catalyst. These features are attributed as future perspectives for the processes [8] .

Significantly, they are also employed for light-induced electron transfer redox reactions towards cycloadditions reactions.[9] MMT is considered to be one of the most promising supports due to its unique properties such as lamellar structure, high cation exchange capacity (CEC), thermal stability and a less expensive choice. The logic behind Montmorillonite (MMT); a natural 2:1 type clay containing aluminium phyllosilicates in a layered structure with cation exchange capacity 120 mequiv./100g possesses beneficial adsorption tenedency[10]

We have designed of tailor-made photo catalyst because it is a key step towards improved quantum efficiency and its subsequent utilized it in cycloaddition processes. This strategy may be achieved via tuning the band gap of semiconducting nanoparticles and dispersing them in a media thereby forming a heterogenized nanocomposite. One fundamental obstacle is inability of most common organic molecules to absorb the wavelengths of visible lights that are most abundant in solar spectrum. Many reports from literature envisage that cycloadditions reactions are also carried out in presence of photocatalyst which prompted us to investigate the feasibility of similar work for C-C Coupling reactions. To achive this goal we had started this project with literature survey of the organometallic reagents and photo catalytic reactions related to the phocatalysis.

Purchase of required chemicals, glassware, and equipments such as rotavapor, magnetic stirrers was made for smooth conduct of research work. Designing and preparation of photo catalyst such as semiconducting nanocomposites such as CdSe/PANI, CdSe/MMT which was used for C-C coupling reactions but it was failed to bring out the conversion. We had used same semiconducting nanocomposite in visible light as catalyst towards formation of C-S and C-N bonds wherein significant conversions are achieved. We had prepared the Ru(bipy)3/MMT nanocomposites for the synthesis cycloadduct as promising photocatalyst wherein we obtained better results. Characterizations of photocatalyst using XRD, SEM, TEM, techeniques. After successfully synthesis and characterization of $Ru(bipy)_3$/MMT , We devised strategy to employed same material for solar light mediated cycloadditon reaction i.e our one of the prime objective of the project. Using such a methodology we got promising results with better conversions with good yields. This simple approach also ensures separation of catalyst by centrifugation method with easy work up and products are obtained by isolated yields. Therefore this methodology may be regarded as simple and greener approach.

Part B: Catalyst characterization and result and Discussions.

2 Characterization of Catalyst

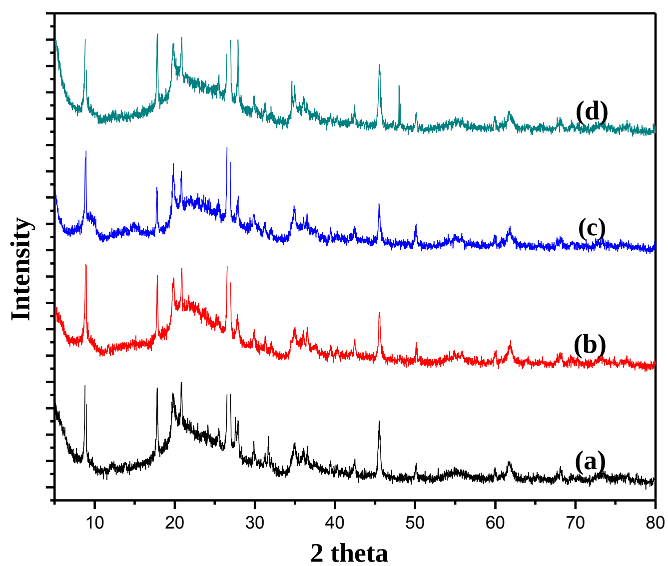


Fig. 3 :XRD patterns of: a) montmorillonite clay, b) 5% $Ru(bpy)_3]^{2+}$/MMT, c) 10% $Ru(bpy)_3]^{2+}$/MMT, d) 15% $Ru(bpy)_3]^{2+}$/MMT

XRD diffraction pattern of pure $Ru(bpy)_3Cl_2$ gives diffraction peaks at 2θ values of 17.6°, 26.0°, 28.1°, 29.1°, 31.0°, 39.4°, 44.4°, 46.4°, 54.5°, 62.5° and 71.6° due to various planes of crystalline complex **(A novel Ru@TiO_2 hybrid nanocomposite for photoreduction).**

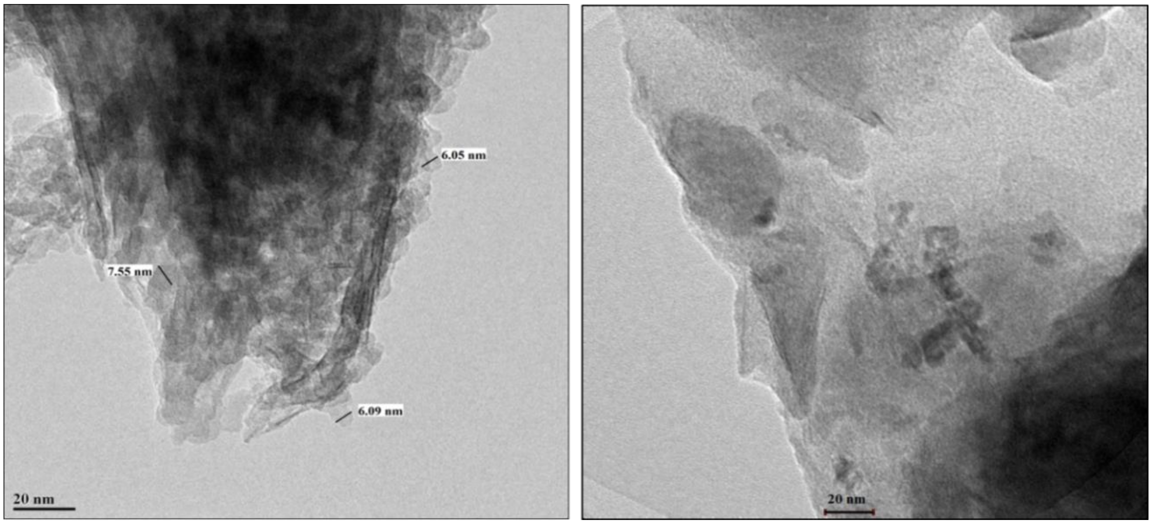


Fig4 :TEM images of $[Ru(bpy)_3]^{2+}$/MMT: a) Fresh b) reused photocatalyst.

1.3 Reusability studies

The main advantage of heterogeneous catalyst is its reusability. As shown in the mechanism , the catalyst should be regenerated and recycled at the end of cycle and hence can be reused. Every cycle resulted in almost sustain catalytic activity with significant conversion and isolated yields. There is no significant reduction in the isolated yield after each cycle. This indicates catalyst

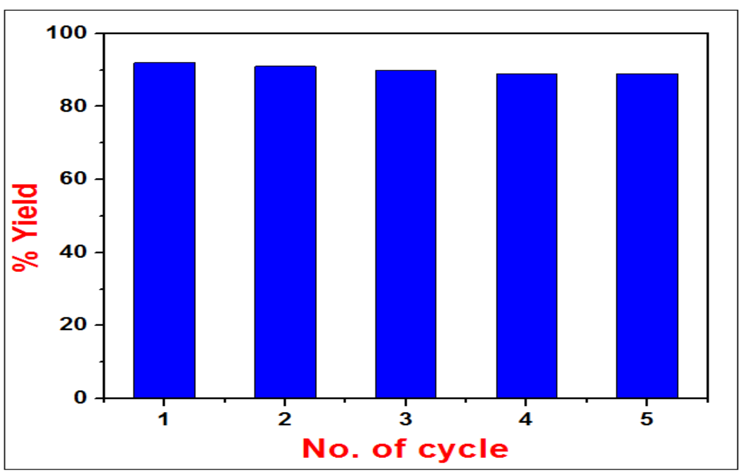


Fig 5 :Reusability studies of $[Ru(bpy)_3]^{2+}$/MMT composite for [2+2] photocycloadditions

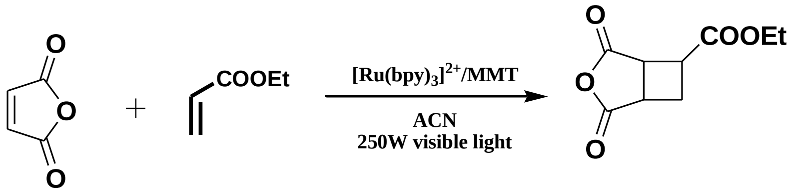
Reaction conditions:

2 mmol of 1, 4- Maleic anhydride, 2 mmol of enoene, 10 mg of 10% $[Ru(bpy)_3]^{2+}$/MMT**,** 50 mL Acetonitrile, 250 W visible light, Time - 4.5h, rt

Sustains its activity even after five consecutive cycles s. The sustained photocatalytic activity is a result of regeneration of Ru^{2+} species from its photo-redox Ru^{3+} state.(as shown in the figure).

Fig 6: Photocatalytic reactor

1.4 Optimization of reaction parameters :



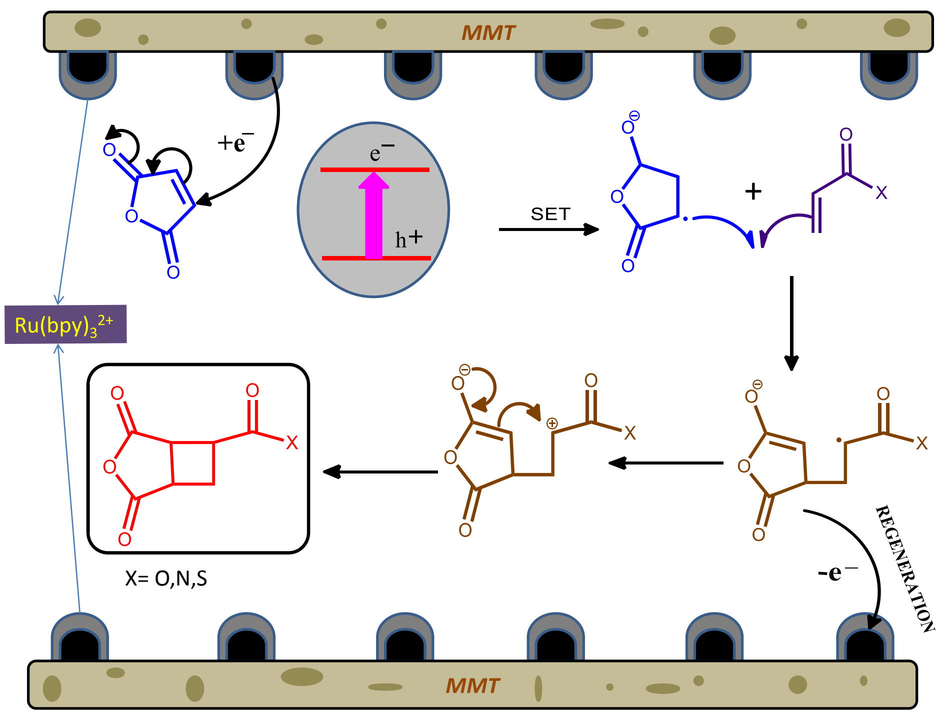
Reaction conditions: Reactants (2 mmol each), Solvent – Acetonitrile (50 mL), Lamp – 250 W visible light, Time – 4 h

1.6 Result and Disscusion

Mechanistic views

The absorption of visible light by catalyst, its photo-excitation and transfer of energy to the substrate, generation of radical intermediates and finally the formation of cycloadduct forms the basis of this photocatalytic organic transformation. The above mentioned maleic anhydride and enone photocycloaddition intitiated with adsorption of substrates by MMT surface. The $[Ru(bpy)_3]^{2+}$ complex is activated and converted to photo-excited* species through absorption of a photon (λ = 453 nm). Photo-emission occurs by ejection PSET i.e. photoexiciated single electron transfer from the catalyst surface that is absorbed by maleic anhydride (good electron acceptor) resulting in the formation of a radical anion on maleic anhdride moiety . This is followed by nucleophilic attack of the anion Michael's 1, 4- addition giving rise to radical anion intermediate (as shown in figure below).

1.7 Proposed mechanism



Conclusion: simple strategy is developed wherein designing of efficient heterogeneous catalyst $Ru(bipy)_3$@MMT was developed under solar and visible light for C-C coupling reactions.

Outcome of Project:

1 .Designing of Ru(bipy)$_3$@MMT as a photocatalyst for the cycloaddition and C-C couplings.

2.Use of visible and solar light for organic transformations.

3.Enrollment/ Registration for Ph.D.

4.Development of practical skills of M.Sc project students.

5. Development in instrumentations/infrastructure facility at college level.

6. synthesis and characterization of compounds.